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Ultrasonic study of 2-butanol in cyclohexane with toluene

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Abstract . The ultrasonic velocity, density and viscosity at 303, 308 and 313 K have been measured in the ternary system of 2-butanol in cyclohexane with toluene The acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure at the said temperatures are calculated The results are interpreted in terms of molecular interaction between the component of the mixtures The existence of weak interactions are confirmed by the observed excess values

Keywords . Ultrasonic velocity, acoustic parameter, dipolar and dispersive interactions.

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1. Introduction

Velocity of sound waves in a medium is fundamentally related to the binding forces between the atoms or the molecules. The variations of ultrasonic velocity and related parameters, throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components [1–3] as well as strongly interacting components [4–6]. Though, a number of investigations were carried out in liquid mixtures having alcohol as one of the components, ternary system with iso-alcohols as one of the component are indispensable for the industrial rectification column to avoid the formation of azeotropes. The present work deals with the measurement of ultrasonic velocity and computation of related parameters in the ternary system of cyclohexane + toluene + 2-butanol at three different temperatures 303, 308 and 313 K.

2. Experiment

The mixtures of various concentration in mole fraction are prepared by taking purified AR grade samples at 303 K. In all the mixtures, the mole fraction of the second component, toluene, was kept fixed, while the mole fraction of the remaining two were varied from 0.0 to 0.6 so as to have the mixtures of different composition.

The ultrasonic velocity in the mixtures is measured using a variable path ultrasonic interferometer working at 2 MHz. The density and viscosity are measured using pycknometer and an Ostwald's viscometer respectively.

Using the measured data, the acoustical parameters, such as adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) and their excess parameters have been calculated using the following expressions.

$$\beta = (U^2\rho)^{-1}, \tag{1}$$

$$L_f = K_T\beta^{1/2}, \tag{2}$$

$$V_f = \left(\frac{M_{\text{eff}}U}{\eta K}\right)^{3/2} \tag{3}$$

$$\pi_i = bRT\left(\frac{K\eta}{U}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{\text{eff}}^{7/6}}\right), \tag{4}$$

$$A^E = A_{\text{expt}} - A_{id}, \tag{5}$$

and $$A_{id} = \sum x_i A_i. \tag{6}$$

where the notations have the usual meaning.

3. Results and discussion

The experimental values of density, viscosity and velocity at 303, 308 and 313 K for the pure components and for the system cyclohexane + toleuene + 2-butanol are given in

Table 1. Values of density (ρ), viscosity (η) and velocity (U).

Mole fraction		ρ kgm^{-3} Temperature (K)			$\eta \times 10^3$ Nsm^{-2} Temperature (K)			U ms^{-1} Temperature (K)		
x_1	x_3	303	308	313	303	308	313	303	308	313
1 000	0 000	767 7	762 7	757 8	0 8003	0 718	0 6673	1230 3	1212 5	1189 1
0 000	0 000	857.8	854 9	851.7	0 526	0 4985	0 471	1287 2	1273.6	1253 5
0 000	1 000	794 5	792 7	787 9	2 195	1 989	1 804	1185	1161	1150 2
0 501	0 098	799 48	796 29	789 72	0 5868	0 5308	0 4981	1215	1198 7	1184 1
0 400	0.200	804.53	797 23	793 14	0 6091	0 5466	0 5066	1206 9	1188 0	1182 24
0 300	0 300	807 82	801 5	797 59	0 6353	0.5714	0 5297	1199.5	1183 1	1180 4
0 200	0 400	809 84	806 99	803 37	0 6719	0 6106	0 5696	1205 3	1195.2	1179 06
0 100	0 499	815 22	812 38	805 59	0 7371	0 6623	0 6073	1210	1199 6	1192 2
0 000	0.5997	818 64	814 62	808 32	0 7582	0 7044	0 6323	1212	1202.4	1196 4

Table 2. Values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i)

Mole fraction		$\beta \times 10^{10}$ Pa^{-1} Temperature (K)			$L_f \times 10^{10}$ m Temperature (K)			$V_f \times 10^7$ m^3 mol^{-1} Temperature (K)			$\pi_i \times 10^{-6}$ Pa Temperature (K)		
x_1	x_3	303	308	313	303	308	313	303	308	313	303	308	313
1 000	0 000	8 6057	8 9183	9 3327	0 5853	0 6006	6202	1 662	1 9135	2 0741	400 08	386 33	380 56
0 000	0 000	7 0359	7 2113	7 4725	0 5293	0 5401	0 5551	3 8238	4 1224	4 3367	307 2	304 93	302 86
0 000	1 000	8 9633	9 3589	9.5936	0 5974	0 6153	0.6288	0 2859	0 3214	0 3669	801 09	781 95	757 26
0 501	0 098	8 4731	8 7399	9.0312	0 5808	0 5946	0 6101	2 6999	3 0755	3 3218	343 73	333.67	328 67
0.400	0 200	8 5332	8 8876	9 0207	0 5829	0 5996	0.6098	2 4837	2 8529	3 1745	357 69	345 08	337 26
0.300	0 300	8.6037	8 9137	8 9983	0 5853	0.6005	0 609	2 2693	2 606	2 9098	372 56	359 74	351 24
0 200	0 400	8 4998	8 6746	8 9539	0 5817	0 5924	0 6075	2 0643	2 353	2 5588	388 22	376 89	371 34
0 100	0 499	8 3783	8.5539	8 7334	0 5775	0.5882	0 5999	1 7651	2 0565	2 3206	413 45	399 16	387 46
0 000	0 5997	8 3157	8 4907	8 643	0 5753	0 586	0 5968	1 6742	1 8475	2 1561	426 16	417 83	401.22

Table 1. The respective calculated values of adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) at different temperatures are given in Table 2. The excess values corresponding to each of the said parameters, are shown graphically in Figures 1 to 4.

The perusal of Table 1 shows that the ultrasonic velocity initially decreases with increasing concentration of 2-ol, attaining a minimum at 0.3 mf of 2-ol and then increases with further increase in concentration. The presence of extremum in the variation of ultrasonic velocity with concentration of

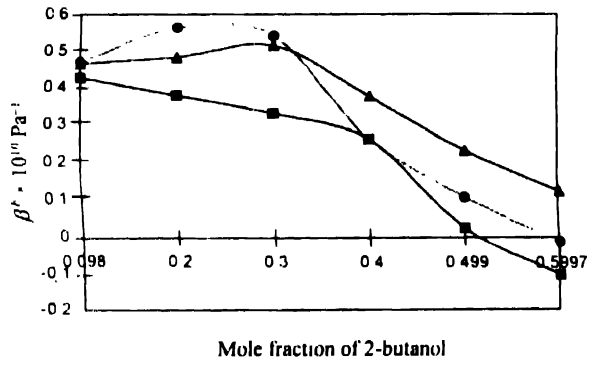

Figure 1. Mole fraction *vs* excess adiabatic compressibility
▲ 303 K, ● 308 K; ■ 313 K

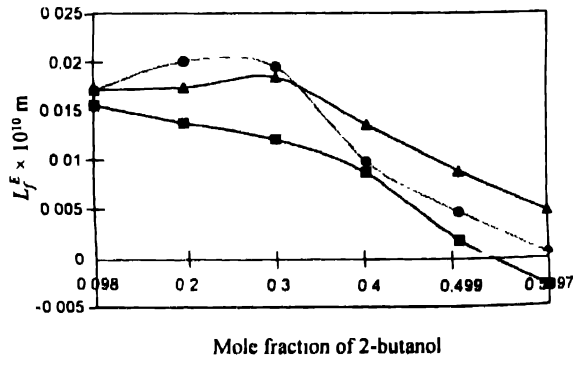

Figure 2. Mole fraction *vs* excess free length
▲ 303 K, ● 308 K; ■ 313 K

2-ol reveals the existence of intermolecular dissociation [7]. Similar behaviour in ultrasonic velocity has been observed by Palaniappan [8] in 1-propanol + cyclohexane + benzene system and by Anbananthan *et al* [9] and Sosamma *et al* [10]

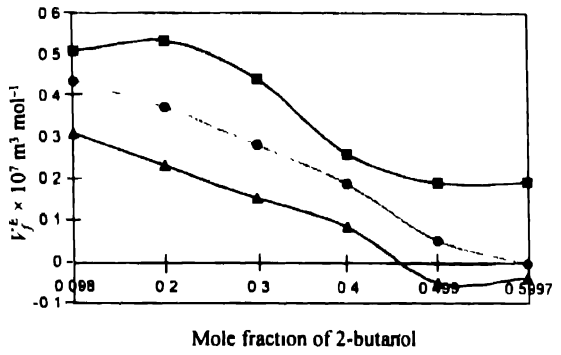

Figure 3. Mole fraction *vs* excess free volume
▲ 303 K, ● 308 K, ■ 313 K

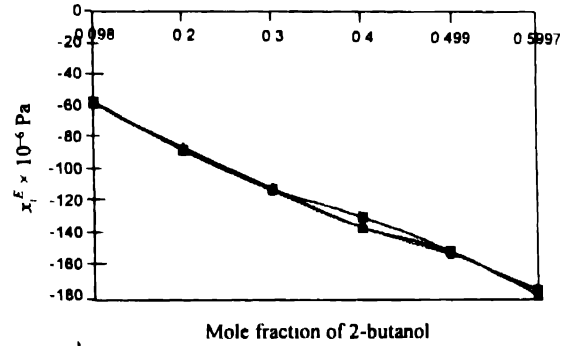

Figure 4. Mole fraction *vs* excess internal pressure
▲ 303 K, ● 308 K, ■ 313 K

in some liquid systems. The adiabatic compressibility and free length shows an exactly reverse trend at 303 and 308 K. But at 313 K, these parameters simply decreases with increasing concentration of iso-butanol. This may be attributed to the fact that by reduction of cyclohexane, rupture of hydrogen bonds decrease and hence the free space between the component molecules and also the field around the charges increase, that makes the medium under heavy stress. As the effect of temperature is to rarefying the medium, the sound velocity with temperature decreases whereas the compressibility increases and so for the free length.

As cyclohexane is having zero dipole moment and as toluene is an electron donor whereas the 2-ol as electron acceptor, some complex formation is expected to take place among the components. Cyclohexane exists in rigid chair form (minimum potential energy), in flexible boat form (maximum potential energy) and also in skew-boat form [11]. Further, the potential energy barrier is not high enough to prevent their rapid interconversion at room temperature or to make possible their isolation [12]. Due to the presence of bowspirit-flagpole interaction in the boat cyclohexane [13], breaking up of hydrogen bonds are highly favoured whereas in chair form it is not so. Hence, depending on the way in which the charge is distributed, the complex formation may interact with the inert cyclohexane molecules. The addition of 2-ol, which is highly polar may reduce the complex formation tendency and so, initially, ultrasonic velocity decreases. However, as the mole fraction of cyclohexane decrease, the rupture of hydrogen bonds are restricted and hence the free space between the component molecule decreases. These two opposing effects compensate each other to different degrees throughout the entire mole fraction range. These effects are reflected in the observed free length variation. The rise in temperature makes the free length to increase, as expected due to the thermal expansion of the liquid medium [14].

Further, as the concentration of 2-ol increases, it is noted that the free volume decreases whereas the internal pressure increases due to the various degree of dispersive interaction and the coulombic interaction existing between the component molecules. Since π_i is a measure of intercomponent forces of attractions, its value is found to decrease with temperature at almost all concentrations of 2-ol studied.

The excess parameters play a major role in understanding the nature of molecular interaction in liquid mixtures. From the Figures 1 and 2, it is clear that at 303 and 308 K as the concentration of 2-ol increases, β^E and L_f^E increases initially, reaches a maximum and then decreases. These trends suggest the presence of specific interaction between the different components of the mixture. The decreasing nature of these parameters at 313 K may be due to the aforesaid stressed media conditions. Figure 3 shows that the values of excess free volume are positive and decreases with increasing concentration of 2-ol whereas the variation in internal pressure (Figure 4) shows an exactly reverse trend. This is attributed to the weakening of dipolar interactions [15] between the molecules of mixtures and shows the absence of complex formation. Similar observations, arrived by Gama and Tojo [16] in the same system by vapour-liquid equilibria studies, supports this view.

4. Conclusion

The derived acoustical parameters and their positive excess values hint to the presence of weak dipolar and dispersive interactions between the component molecules in the mixtures studied and the inherent nature of alcohols predominate the existing dispersive interactions.

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